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THE CATALYTIC PARTIAL OXIDATION OF ETHYL ALCOHOL

BY

DONALD B. KEYES

AND

ROBERT D. SNOW

BULLETIN No. 238

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BULLETIN NO. 238 NOVEMBER, 1931

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BY

DONALD B. KEYES

PROFESSOR OF INDUSTRIAL CHEMISTRY

AND

ROBERT D. SNOW

SPECIAL RESEARCH ASSISTANT PROFESSOR
IN CHEMICAL ENGINEERING

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THE CATALYTIC PARTIAL OXIDATION OF ETHYL ALCOHOL

I. Introduction

1. *Importance of Partial Oxidation.*—It is not necessary to point out the importance of synthetic organic chemical manufacture in this country and in foreign countries. It is interesting to note, however, that a great many of our synthetic products are pure compounds containing not only the elements carbon and hydrogen but also oxygen. This at once indicates that it might be possible to synthesize a great many of our valuable organic compounds by reacting the raw material, for example, a hydrocarbon with ordinary atmospheric oxygen. In brief, a successful application of partial oxidation would contribute to the more economical production of many of our solvents, industrial organic chemicals, and intermediates for dyes, medicinals, and pharmaceuticals.

At the present time this is not done except in a very few isolated cases. Usually the synthesis is extremely complicated, consisting of several steps and though the raw material is inexpensive, the final product is often very costly.

Such a single step in partial oxidation, as has been suggested, is thermodynamically possible but it is extremely difficult. The outstanding difficulty is the question of proper heat transmission. In order to get the oxidation to stop at the required point it is necessary to control the temperature of the reaction within a few degrees. If the vapor phase is utilized for these oxidations there is nothing present to absorb the heat given off by the reaction except the reacting gases. These usually have low specific heats with the result that the heat is not transmitted away from the scene of reaction at a sufficient speed to prevent the temperature from rising to a point that is disastrous for the particular reaction desired.

If the liquid phase is used, however, the greater heat capacity of the liquid present serves to eliminate some of this difficulty. Two new difficulties, however, appear. One is the difficulty of obtaining satisfactory contact between the gas, air, and the organic liquid. Another difficulty is that most of these reactions, if carried out in the liquid phase, must be carried out at a low temperature to prevent the liquid from boiling. It is impractical to utilize pressure in an oxidation because of the danger of explosions. The catalysts worked with

in our scientific and industrial laboratories have practically all been for vapor phase oxidation and are catalysts that function only at relatively high temperatures. This means that partial oxidation studies carried out in the liquid phase will first of all require the development of catalysts that will operate in the liquid phase and at low temperatures.

Some years ago, at the University of Illinois, in starting this investigation the oxidation of acetaldehyde to acetic acid was studied.* This is a relatively simple reaction to carry out in the liquid phase. It did, however, give some indication as to the type of catalyst necessary for this type of work.

A study was also made on contact machines for liquid gas reactions in order to find out the best type of laboratory apparatus for this liquid phase partial oxidation.†

In order to continue the catalytic study the oxidation of alcohol to acetaldehyde and acetic acid was next selected. This bulletin will cover the results of this particular investigation.

2. *Acknowledgments.*—The authors desire to acknowledge the many suggestions given by DR. SHERLOCK SWANN, JR., Research Associate in Chemical Engineering at the University of Illinois, as well as the assistance of MR. L. H. ROSENFELD, student, who carried out the pressure experiments.

The investigation described in this bulletin was conducted by the Engineering Experiment Station of the University of Illinois, of which DEAN M. S. KETCHUM is the director, under the direction of PROF. D. B. KEYES, Head of the Division of Industrial Chemistry.

This investigation was made possible by the generous financial aid given by the Chemical Foundation, New York City, of which MR. FRANCIS P. GARVAN is president, and MR. W. W. BUFFUM is general manager and treasurer.

II. HISTORY OF OXIDATION OF ALCOHOL

3. *Vapor Phase.*—The chemical literature contains numerous references to the vapor phase oxidation of ethyl alcohol. In most of these investigations and processes a mixture of air or oxygen with alcohol vapor is passed at a pressure near atmospheric over a catalyst heated to temperatures within the range 200 to 400 deg. C. In the majority of cases the catalyst consists of some form of copper or copper oxide, either alone or in combination with other metals or

*King, Swann, and Keyes, Ind. Eng. Chem., 21, 1227, 1929.
†Univ. of Ill. Eng. Exp. Sta. Cir. 19, 1929.

oxides. Other materials mentioned as single catalysts or as components of catalytic mixtures are those of silver, zinc, manganese, vanadium, cerium, cobalt, molybdenum, tungsten, chromium, iron, and platinum, or their oxides. The reaction product is a mixture of water, carbon dioxide, aldehyde, and acid in which the acetaldehyde obtained may be as high as 66* to 78 per cent† but the acetic acid is never more than 3 per cent of the theoretical yield from the alcohol converted. In order to obtain profitable yields of acetic acid it is necessary to purify the acetaldehyde by fractional distillation or by other means; it may then be subjected to a further oxidation in the liquid phase, as done by the Canadian Electrochemical Products Company, or to a chemical oxidation in the vapor phase by Cu_2O_3 as proposed by Hale and Haldeman.‡ The patent literature appears to favor the liquid phase process.

4. *Liquid Phase.*—

(a) By Air or Oxygen

References in the chemical literature to the liquid phase partial oxidation of alcohols by air or oxygen are very rare. This is remarkable because undoubtedly there have been many attempts to carry out this reaction.

Calvert§ observed that during a period of 72 hours a considerable quantity of acetic acid was formed when a few drops of ethyl alcohol were in contact with charcoal which had previously been heated to redness and then cooled in a cylinder filled with oxygen.

Mathieu¶ observed that air will oxidize an alcohol solution when chemical agents such as SO_2, $FeSO_4$, FeO, and MnO_2 are present. The action is aided by sunlight.

Duchemin and Dourlen** obtained about 0.2 per cent conversion to acid by boiling alcohol with granulated copper under a reflux condenser. They assumed a two-stage mechanism, first, a catalytic dehydrogenation to aldehyde by copper, and second, an oxidation of aldehyde to acid by dissolved air.

Glaessner†† produced formaldehyde by passing air at room temperature through solutions of colloidal platinum or colloidal copper containing methyl alcohol.

*Orloff, J. Russ. Phys. Chem. Soc., 40, 203, 1908.
†Simington and Adkins, J. Am. Chem. Soc. 50, 1449, 1928.
Naumann, Moeser, and Lindenbaum, J. prakt. Chem., 75, 146, 1907.
Karpov, Zhur. Prikl. Khim. 1, 121-6, 1928.
Lowdermilk and Day, J. Am. Chem. Soc., 52, 3535, 1930.
‡Hale and Haldeman, Brit. Pat. 287,064; French Pat. 650,771.
§Calvert, J. Chem. Soc., London, 20, 293-6, 1867.
¶Mathieu, Chem. Zentr. 2, 782, 1905.
**Duchemin and Dourlen, Compt. rend., 139, 681, 1904; 140, 1466, 1905.
††Glaessner, Chem. Zentral. II, 731, 1902, Oester. Chem. Ztg. 5, 337.

Doroshewski and Bardt* concluded that the oxidizing action of activated charcoal on alcohol is due to the adsorbed oxygen. They found that dilute solutions are oxidized more easily than are concentrated solutions and that the principal product is acetaldehyde, with only a small amount of acid.

Lamay and Jalouster† found that such organic compounds as adrenaline and morphine in dilute solutions are rapidly oxidized catalytically by small amounts of the bromide of thorium X. Under similar conditions ethyl alcohol is not oxidized.

(b) Induced Oxidations

Cohen and Boeseken‡ have studied the oxidation of alcohol to acetaldehyde induced by photoactive aromatic ketones.

Ciamician and Silber§ found that the oxidation of alcohol to acetaldehyde was induced by the oxidation of xylene and certain aldehydes, ketones, and quinones, by air in sunlight.

Steedman¶ observed that air in the presence of turpentine oxidized alcohol slowly to acetic acid during a period of months.

Mittra and Dhar** found that air oxidation of Na_2SO_3 or suspensions of freshly precipitated $Fe(OH)_2$ in solutions containing alcohol, induced the oxidation of alcohol to aldehyde and CO_2.

(c) By Chemical Oxidizing Agents

The oxidation of alcohol by many chemical oxidizing agents has been studied. For convenience, some of the results are shown in Table 1.

In a majority of cases acetaldehyde is mentioned as the chief product. However, even if a good yield of acetic acid could be obtained, the cost of most chemical oxidizing agents would render such a process impractical at the present time.

(d) By Electrochemical Methods

Rather complete investigations of the electrolytic oxidation of alcohol have been made. A current yield of about 75 per cent, and a chemical yield of from 77 to 94 per cent have been reported.†† Haberman‡‡ and Dony Henault§§ found that acetaldehyde was produced by

*Doroshewski and Bardt, J. Russ. Phys. Chem. 46, 754-85, 1914.
†Lamay and Jalouster, Compt. rend. 174, 171-2, 1922.
‡Boeseken and Cohen, Proc. Acad. Sci., Amsterdam, 18, 1640-7, 1916.
Cohen, *ibid.*, 26, 443-55, 1923.
Boeseken, Rec. trav. chim. 40, 433-45, 1921.
§Ciamician and Silber, Ber. 46, 3894, 1913; 46, 417-22, 1913; 45, 38-43, 1912; 33, 2911, 1900; 36, 1575, 1903.
¶Steedman, Chem. News 55, 270, 1887.
**Mittra and Dhar, Z. anorg. allgem. Chem., 122, 146-50, 1922.
††Muller and Rius, Z. Elektrochem. 27, 54, 563, 1921.
Askenasy, Leiser and Grunstein, Z. Elektrochem. 15, 846, 1909.
‡‡Haberman, Monats. für. Chem. 7, 533, 1886.
§§Dony Henault, Z. Elektrochem. 6, 533, 1900.

TABLE 1
OXIDATION OF ALCOHOL BY CHEMICAL OXIDIZING AGENTS

Oxidizing Agent	Products	Reference
Sb_2O_5	Acetaldehyde	Trillat, Bull. Soc. Chim. 3, 17, 230, 1897.
Bi_2O_3	Acetaldehyde	Trillat, Bull. Soc. Chim. 3, 17, 230, 1897.
HgO MnO_2	Acetic acid CO_2	Beilstein, Book 1, 302, 1918.
Ozone	Acetic acid, formic acid, oxalic acid	Wright, Amer. Jour. of Sci., 3, 7, 184.
Ozone	Peroxide ($C_2H_5O_2OH$—aldehyde + H_2O_2	Harries, Liebig's Ann., 374, 288, 1910.
Ozone	Acetaldehyde and acetic acid	Hougean, Compt. rend., 75, 142.
Hydrogen peroxide	Acetaldehyde	Stoecklin, Compt. rend., 148, 424, 1909.
$H_2O_2 + Fe_2(SO_4)_3$	Aldehyde + CO_2	Walton and Christensen, Jour. Amer. Chem. Soc., 48, 2083, 1926.
$HClO_3$ $HBrO_3$	Acetic acid, ethyl acetate	Serullar, J. de chim. Med., 33, 1831.
HNO_3 cold	Acetic acid	Bird, Phil. Mag., 324, 1839.
HNO_3	Oxalic acid, glycolic acid, glyoxalic acid, acetic acid	Bottinger, Arch. Pharm., 232, 65.
Mn_2O_3	Aldehyde	Lang, U. S. P. 808, 095, 1905.
$KMnO_4$	Acetic acid	Evans and Day, Jour. Amer. Chem. Soc., 38, 375, 1916; 41, 1267, 1919.
$KMnO_4 + NaOH$	Acetic, oxalic and carbonic acids	de Bruyn, Ber. 26, 270, 1893.
$KMnO_4 + H_2SO_4$	Acetaldehyde + acetic acid	Chapman, Jour. Chem. Soc., 20, 301, 1867.
$MnO_2 + H_2SO_4$	Acetaldehyde, diethyl acetal	Wurtz, Annales (3), 48, 370, 1856.
Cr_2O_3	Acetic acid	Boureart, Mulh, 59, 558.
Cr_2O_3	Acetaldehyde	Boettger, Ann. de Pharm. 37, 117; 57, 134, 1846.
Cr_2O_3	Acetaldehyde, acetic acid, diethyl acetal	Rogers, Jour. prakt. ch. (1), 40, 240, 1847.
Persulphate	Acetaldehyde	Namias, Chem. Zentral, (2), 806, 1900.
Pernitric acid	Acetaldehyde	Trifonow, Z. anorg. allgem. chem., 124, 136, 1922.

electrolysis of alcohol containing H_2SO_4, and aldehyde resin from alcohol containing sodium ethylate. Renard,* and Elbs and Brunner† obtained principally acetic acid, with some aldehyde, by electrolyzing alcohol containing H_2SO_4.

Commanducci‡ subjected a mixture of alcohol vapor and air to a non-luminous electrical discharge and obtained chiefly acetaldehyde.

*Renard, Annales 151, 17-289, Chem. Zentral. 565, 1879.
†Elbs and Brunner, Z. Elektrochem. 6, 604, 1900.
‡Chem. Zentral. I, 1530, 1909.

III. Theoretical Discussion

5. *General.*—Thermodynamical considerations predict that a reaction is possible when it is attended by a loss of free energy.

In the case considered there are three main reactions:

(1) $C_2H_5OH + \frac{1}{2}O_2 \longrightarrow H_3CCHO + H_2O$

(2) $C_2H_5OH + O_2 \longrightarrow H_3CCOOH + H_2O$

(3) $C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$

all of which take place with a loss of free energy, so that all three reactions are possible. Not all reactions, however, which are thermodynamically possible actually take place spontaneously with a noticeable velocity. Thermodynamics does not predict which of a group of possible reactions will take place nor with what velocity.

In order that a thermodynamically possible reaction may take place, two conditions must be satisfied: first, there must be molecular collisions between the reactants; and, second, the molecules must be activated with sufficient energy to overcome the natural inertia to chemical change. The first requisite (molecular collisions) involves only the relatively simple mechanical problem of bringing the two compounds into intimate contact by mixing or solution, and need not be considered further. The second requisite, that of activated molecules, is the real controlling factor in most reactions. Not all molecules within a system have the same energy content. Usually only a very few have sufficient energy to react, *i.e.*, are activated. Chemical reaction involves these activated molecules, and the velocity of the reaction depends upon the number of activated molecules. Promoting the reaction, then, becomes a matter of activating a sufficient number of molecules.

6. *Activation by Heat-Temperature.*—Heat energy absorbed by molecules as the temperature of the reaction mixture is raised is distributed as increased energy of translation and increased energy of the various forms of internal vibrations and orbital velocities, with the result that the molecules become more unstable toward chemical change, *i.e.*, they become more reactive. The general effect of higher temperature is increased velocity of chemical reaction; in fact, it is found that in a large number of cases, the velocity is doubled when the temperature is raised 10 deg. C.

In carrying out the liquid phase partial oxidation of ethyl alcohol, it is necessary to operate at a temperature below 78.4 deg. C., the

boiling point at atmospheric pressure, or, if a higher temperature is used, to apply sufficient pressures in order to maintain the liquid phase. The use of higher pressures is not desirable, however, on account of the danger of explosions. To a limited extent, a higher temperature could be maintained at atmospheric pressure by the use of an inert solvent of high boiling point, but the active concentration of alcohol would be reduced proportionately.

One very serious disadvantage of thermal activation of organic molecules is that all of the bonds are loosened and, in addition to the accelerating effect on the desired reaction, the velocities of numerous undesirable side reactions are increased to a greater or less degree. Thus, in the vapor phase oxidation of alcohol, it is found that higher temperatures favor the complete oxidation to CO_2 and H_2O rather than the partial oxidation to aldehyde and acid.

7. *Catalytic Activation.*—A catalyst is a substance which can modify the velocity of a reaction without itself undergoing a permanent chemical transformation. If, as frequently happens, the catalyst enters into chemical reaction with one or more of the reactants to form transitory intermediate compounds, it is regenerated in its original chemical form in the final stage of the cycle. By repetition of this cycle a small amount of catalyst is able to effect the conversion of an indefinitely large amount of the reactants.

The catalyst probably functions by selectively straining and loosening those bonds of the molecule which will permit the reaction to take place. Catalysts are able to perform this function under conditions of abnormally low thermal activation (lower temperatures); hence, the heat of activation is much smaller. For example, a mixture of H_2 and O_2 is stable at rather high temperatures, but is readily ignited by a platinum sponge at ordinary temperatures. Since catalysts are selective in their action, the reaction can be controlled by them to give the desired product also. There is evidence in many cases that the catalyst first reacts with one of the reacting compounds to form an intermediate compound, which subsequently reacts with the other reacting compound with the regeneration of the catalyst.

$$A + O_2 \longrightarrow AO_2 \qquad AO_2 + 2B \longrightarrow 2BO + A$$

Thus, the mechanism of the catalytic oxidation of alcohol to aldehyde in the presence of osmium dioxide is

$$OsO_2 + O_2 \longrightarrow OsO_4 \qquad \text{Intermediate compound}$$

$$OsO_4 + 2C_2H_5OH \longrightarrow 2HC(H)(H) - C = O + 2H_2O + OsO_2$$

Catalysts are of two classes, homogeneous and heterogeneous, depending upon whether the catalyst is in the same phase with the reactants or not. Thus, oxides of nitrogen are homogeneous catalysts for the vapor phase oxidation of alcohol, while copper is a heterogeneous catalyst for the same reaction. The efficiency of promoting a reaction as evidenced by the reaction velocity should be proportional to the concentration of a homogeneous catalyst. On the other hand, the efficiency of the heterogeneous catalyst depends more upon the physical state, *i.e.*, fineness of division, character, and extent of surface, than upon the mass of the catalyst. This is due to adsorption of gases or liquids on the surface of the solid and to an activation of the atoms composing the layer next to the surface of the solid.

In the search for a catalyst for the oxidation of alcohol, those soluble compounds which form addition compounds with alcohol or with oxygen should be tested as possible homogeneous catalysts. Examples of the first type are calcium chloride and sulphuric acid, and of the second type are salts of metals which can change their state of oxidation. Solid materials such as activated charcoal and silica gel which are known to have active surfaces should be tested as possible heterogeneous catalysts.

The best method of promoting the desired reaction is to use a catalyst which will overcome the inertia to, or impediments of, reaction and loosen only those bonds of the molecule required for the reaction to take place. The operating temperature, *i.e.*, thermal activation, should then be maintained at the lowest point at which the reaction progresses at a practical rate.

8. *Induced Oxidation—Autoxidation.*—Several cases have been observed in which the oxidation of one compound (A) brings about the simultaneous oxidation of another compound (B) which is capable of oxidation but which under most other conditions (in the absence of the system which is promoting the reaction) would remain unchanged in the presence of the oxidizing agent. Thus, for example, ethyl alcohol, exposed to the simultaneous action of sunlight and air, is not appreciably changed, but in the presence of xylene which is oxidized, the alcohol goes slowly to acetic acid. Such coupled reactions are called induced oxidations; (A) is the inductor and (B) the acceptor.

Unactivated molecules of (A) may also act as acceptors. When air or oxygen is the oxidizing agent the phenomenon is termed autoxidation.

Observations of induced oxidations date from the researches of Schonbein,* who found that during the autoxidation of many substances, *e.g.*, turpentine and benzaldehyde, for every molecule of oxygen appearing in the reaction product of the primary substance undergoing oxidation an equivalent amount of oxygen was simultaneously transformed to a more active state. This active oxygen could then react secondarily with more oxygen, forming ozone, with water, forming hydrogen peroxide, or with certain other substances—*e.g.*, indigo blue, thus effecting oxidations which could not be effected by ordinary oxygen.

Schonbein proposed the dualistic theory of Brodie† as an explanation of this phenomenon. This theory states that the oxygen molecule is broken up into two parts of opposite charge. Clausius‡ and Van't Hoff§ supported this theory. However, efforts to prove the existence of ozonized oxygen in such systems have not yielded conclusive results, and most of the later experiments have added more and more support to the intermediate compound theory of Traube,¶ Bach,** and Engler.††

According to these investigators, the activation of oxygen takes place through the formation of a peroxide of the primary substance, or inductor, which then transfers a portion of its acquired oxygen to another oxidizable substance, the acceptor, and becomes a normal oxide, thus:

$$\underset{\text{Inductor}}{A} + O_2 \longrightarrow \underset{\text{Peroxide}}{AO_2}$$

$$AO_2 + B \longrightarrow AO + BO$$

This view was supported by the experimental discovery and isolation of peroxides of several substances known to act as inductors. Baeyer and Villiger‡‡ and Bodlander§§ in studying the system air as the actor, benzaldehyde as the inductor, and indigo as an acceptor, isolated the intermediate compound, benzoyl hydrogen peroxide

$$C_6H_5CHO + O_2 \longrightarrow C_6H_5CO{:}O(OH)$$

*Schonbein, Pogg. Ann. 100, 1; 105, 258; 106, 307; 108, 471.
Schonbein, Jour. prakt. Chem. 1858, 1859, 1860, 1864, 1868.
†Brodie, Phil. Trans. 141, 759, 1850; 151, 837, 1862; Proc. Roy. Soc. 11, 442, 1861.
‡Clausius, Pogg. Ann. 103, 644, 1858; 121, 256, 1864; Ber. 15, 2421, 1882.
§Van't Hoff, Z. physik. Chem. 16, 411, 1895.
¶Traube, Ber. 15, 663, 1882; 26, 1471, 1893.
**Bach, Compt. rend. 124, 951, 1897.
††Engler, Ber. Vol. 30, 31, 33, 34, 36, 1897-1903.
‡‡Baeyer and Villiger, Ber. 33, 1569, 2480, 1900.
§§Bodlander, Ahrens Sammlung 3, 470, 1899.

and this peroxide could then react in two different ways:

(a) with another molecule of benzaldehyde

$$C_6H_5CHO + C_6H_5CO{:}O(OH) \longrightarrow 2C_6H_5COOH$$

(b) with the acceptor indigo

$$C_6H_5COO(OH) + \text{indigo} \longrightarrow C_6H_5COOH + \text{isatin.}$$

Further evidence of intermediate compound formation has been obtained by Job* in the case of cerium salts and by Manchot,† Goard and Rideal,‡ and Bohnson and Robertson§ in the case of iron salts.

Moureu and Dufraisse¶ have done a vast amount of very valuable work in the related fields of autoxidation, catalysis, and antioxygenic action. They, also, agree that an intermediate peroxide is formed in all cases of autoxidation, but contrary to previous authors, they believe that this reaction takes place with an absorption of energy from the mass as a whole, instead of a liberation of energy to the surrounding medium. From the results of their many investigations they have drawn the following conclusions:

(1) Anti-catalysis is very general in autoxidations. For example, several phenols and iodine compounds inhibit the oxidation of aldehydes.

(2) The two inverse catalyses, anti-oxygenic and pro-oxygenic, have a common underlying causation due to which a substance may act either as an anti-oxygenic, or as a pro-oxygenic catalyst, depending upon conditions.

(3) The catalytic properties of a substance are related to its susceptibility towards oxidation.

(4) The catalytic activity is centralized in that part of the molecule which is susceptible to oxidation.

Regardless of the mechanism by which induced reaction takes place, it is observed that during the induced oxidation of an acceptor, a definite, usually an equivalent, amount of the inductor is oxidized. In catalytic oxidation, on the other hand, a small quantity of catalyst can promote the oxidation of an indefinite quantity of a substance without itself undergoing change. The relation between induced and catalytic oxidation is worthy of further consideration.

Job** observed the striking phenomenon that the inductor cerous hydroxide brings about the induced oxidation of one acceptor, potassium arsenite, while with another substance, glucose, it brings about catalytic oxidation. Cerous salts dissolved in concentrated aqueous

*Job, Ann. de. Chim. et de Phys. (VII), 20, 205, 1900; Compt. rend. 134, 1052, 1902; 136, 45, 1903
†Manchot, Z. anorg. Chem. 27, 397, 1901; Ber. 34, 2479, 1901.
‡Goard and Rideal, Proc. Roy. Soc. 105, 135, 150, 1924.
§Bohnson and Robertson, J. Am. Chem. Soc., 45, 2493, 1923.
¶Moureu and Dufraisse, Chem. Reviews, 3, 113, 1926; Trans. Far. Soc., 24, 707, 1928.
**Loc. cit.

K_2CO_3 give a colorless solution which, on exposure to air, turns dark red, owing to the formation of a complex carbonate in which cerium exists in the hexavalent state. Ammonium ceric nitrate, on the other hand, gives under similar circumstances a yellow solution which remains unchanged by air. From these observations it appears that the cerous compounds, on oxidation, attain the perceric state directly without passing through the intermediate ceric stage. In the presence of an excess of potassium arsenite, this perceric compound is reduced to the quadrivalent ceric state with the corresponding oxidation of the arsenite to arsenate. This is purely an induced reaction and stops, except for the very slow oxidation of $KAsO_2$, as soon as the cerium salt is all converted to the ceric form. Cerium salts, however, can be made to exert a catalytic effect on the oxidation of potassium arsenite, or a very small quantity of a cerous salt can, under suitable conditions, effect the atmospheric oxidation of an indefinite quantity of potassium arsenite. Job found that the simple addition of glucose to the solution undergoing oxidation was sufficient to convert the reaction from one of the induced type to one of the purely catalytic type. The glucose was able to reduce the ceric salt to the cerous form from which the process could start anew, with fixation of atmospheric oxygen, and continue indefinitely if an excess of glucose was present.

Goard and Rideal* have explained this behavior from the standpoint of the oxidation potentials of the various substances involved in the system. They assume that the potential of an unalterable electrode immersed in the solution of an oxidation-reduction mixture is a measure of the free energy change in the reaction. Then, in the system inductor (A) and acceptor (B) reacting according to the following equations,

$$A + O_2 \longrightarrow AO_2$$
$$AO_2 + B \longrightarrow AO + BO,$$

if the oxidation potentials are in the following order of magnitude,

Increasing oxygen pressure (oxidation potential)

$\longrightarrow$

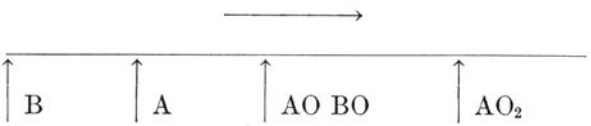
A	B	AO BO	AO_2

an induced oxidation is to be expected. In this case, oxygen, acting upon the inductor (A), raises the oxygen pressure of the solution to a

*Goard and Rideal, Proc. Roy. Soc. 105, 135, 1924.

high value corresponding to the potential of AO_2. As a result, the acceptor (B) is oxidized with the reduction of the peroxide of A to the oxide AO, and a lowering of the oxygen pressure to some intermediate value at which AO and BO exist together in equilibrium. Since the oxygen pressure of A lies below that of B, B will be unable to reduce AO to the initial state A at which fresh peroxide will be formed. Hence, the reaction will stop at the point at which all of the inductor exists in the form of the oxide AO.

If, on the other hand, the potentials observe the following order:



the reaction should be catalytic, since the peroxide AO_2 will be reduced by B to the initial state A, from which the process may be repeated so long as B is present. A will thus be able to fix atmospheric oxygen to an indefinite extent.

The oxidation potentials determined experimentally for the systems cerous, ceric, perceric salts—potassium arsenite, and cerous, ceric, perceric salts—reducing sugars, are of the order of magnitude predicted by this theory.

Probably no induced oxidation of alcohol would be economical on account of the cost of the inductor and of regenerating it. It is possible, though, that a sufficiently cheap reducing material could be found, the addition of which to the oxidizing mixture would reduce the oxide of the inductor, thus effecting a continuous catalytic oxidation of both the alcohol and the reducing agent.

The principal reason, however, for considering in this investigation several substances known to act as inductors for oxidation of other substances was the implication of Rideal's theory that the normal oxides of some of these inductors might have a sufficiently high oxidation potential to oxidize the alcohol, itself, or the aldehyde formed, thus effecting a direct catalytic oxidation without the addition of a more profound reducing agent.

9. *Other Methods of Activation.*—

(a) Electrical Method

Ozone, produced by passing an electrical discharge through air, is a very active oxidizing agent and can oxidize alcohol to acetalde-

hyde. However, the conversion of oxygen to ozone is an endothermic reaction requiring considerable electrical energy at a rather low efficiency. The use of ozonized air would, therefore, be economical only in case the activated oxygen could initiate reaction chains which would promote the reaction of a considerable amount of the unactivated oxygen.

(b) Photochemical Activation

Molecules may be activated by absorption of light energy. The reaction is rather specific in that the active portions of the spectrum are confined within narrow limits of wave length, whereas the energy of most sources of light is distributed more or less evenly over large portions of the spectrum. Hence, the use of any source of artificial illumination would be practical only in case rather long reaction chains were initiated.

IV. Experimental

10. *Preliminary Experiments.*—Since the reaction takes place between a liquid and a gas which is very slightly soluble therein, it is desirable to use some apparatus which will effect intimate contact of the two phases. There has been developed* a turbine-driven, high-speed stirrer for gas-liquid reactions which accomplishes this purpose exceedingly well. The apparatus used in the preliminary experiments was substantially that application of the high-speed stirrer described by King, Swann, and Keyes,† and shown in Fig. 1.

The stirrer was made of illium to resist corrosion by acids. It was driven at a speed of about 5000 r.p.m. by an air turbine. The shaft of the stirrer was about 8 inches long and the flat circular plates forming the slit at the bottom were 2 inches in diameter. The width of the slit between the plates was adjusted to about five one-thousandths of an inch. In operation the stirrer is immersed in the liquid and the gas is slowly passed into the cone at the bottom of the stirrer. Gas and liquid are drawn into the stirrer by the cavitation due to rotation. Here they are intimately mixed by a shearing action while they are being projected through the slit by centrifugal force.

The reaction vessel was a tall form beaker having a capacity of one liter. It was closed at the top by a large rubber stopper coated with latex to minimize the extraction of sulphur compounds from the rubber by the reaction mixture. A practically gas-tight joint between

*Univ. of Ill. Eng. Exp. Sta. Cir. 19, 1929.
†King, Swann, and Keyes, Ind. and Eng. Chem., 21, 1227, 1929.

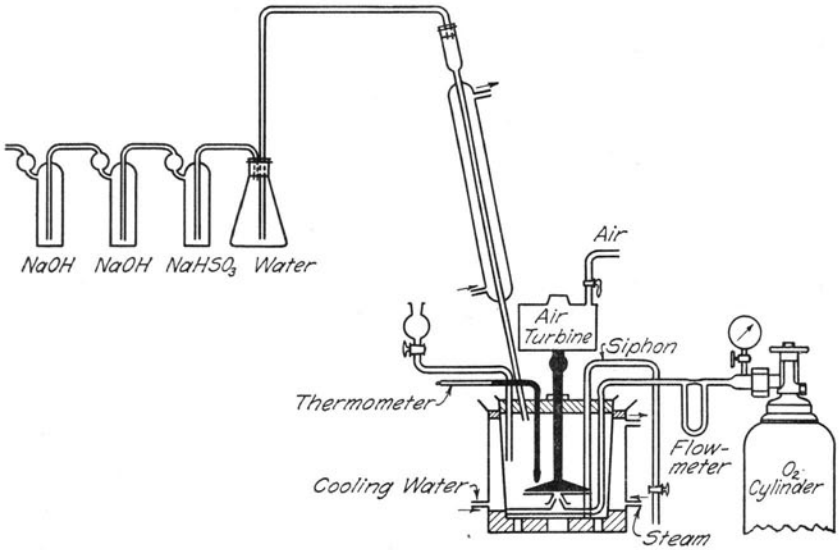


FIG. 1. HIGH-SPEED STIRRER APPARATUS FOR GAS-LIQUID REACTIONS

the rubber stopper and the stirrer shaft was made by a special packing gland. This packing gland consisted of a cylinder machined from hard rubber. It was threaded inside and contained split bushings of hard rubber at the top and bottom. It was packed with asbestos string lubricated with graphite.

The oxygen gas entered the beaker through a glass tube bent to open upward into the cone of the stirrer. Exit gases passed through a reflux condenser to return as much liquid as possible and then through absorption bottles to test for aldehyde and CO_2 formation.

A dropping funnel was provided by which additions could be made to the charge. Samples were removed for analysis by means of a syphon.

The temperature was indicated by a thermometer bent at right angles to clear the turbine and recalibrated. The heating bath consisted of a larger beaker surrounding the reaction vessel and containing water. Heating was done with steam.

Experiment 1

The oxidation of alcohol was attempted under condition in which acetaldehyde is rapidly oxidized by oxygen. The charge, which consisted of 400 cc. glacial acetic acid, 50 cc. of 95 per cent ethyl alcohol, and 5 g. of cobalt acetate, was kept at 70-80 deg. C. and

oxygen was passed through the high-speed stirrer. Samples of 1 cc. each were removed and titrated with 0.959 N NaOH solution using phenol-phthalein as an indicator.

Titration of 1 cc. glacial acetic acid required 17 cc. NaOH.

Titration of 1 cc. of the mixture charged required 15.22 cc. NaOH.

Titration of samples

after 2 hours	14.97 cc. NaOH
after addition of 50 cc. more alcohol	13.59
after 9 hours	12.46
after 18 hours	11.79

The decrease in the acidity of the charge indicates that the principal reaction was esterification. There was no apparent absorption of oxygen at any time.

Experiment 2

A charge of 400 cc. glacial acetic acid, 50 cc. ethyl alcohol, 50 cc. water, and 10 g. vanadium acetate was treated as in Experiment 1.

Titrations of 1 cc. samples at start 13.40 cc.

after 3 hours	12.50
after 7 hours	12.50
after 11½ hours	12.70
after 15½ hours	12.70
after 24 hours	13.17

In this case again there was no detectable oxidation in 24 hours treatment with oxygen at 85 deg. C.

Experiment 3

A charge of 400 cc. glacial acetic acid, 50 cc. ethyl alcohol, 50 cc. water, and 10 g. cobalt acetate was treated with oxygen at 90-95 deg. C. No oxidation to acetic acid could be detected in 24 hours, nor was acetaldehyde found in the wash bottles.

Experiment 4

A charge of 500 cc. ethyl alcohol and 10 g. cobalt acetate was treated with oxygen at 75 deg. C. No oxidation to acetic acid was observed in the 24-hour treatment.

Experiment 5

Since the oxidation of acetaldehyde takes place through the formation of an intermediate peroxide, peracetic acid, of high oxidizing potential, it seemed probable that the autoxidation of acetaldehyde could induce the oxidation of ethyl alcohol. Furthermore, the pink color of a mixture of cobalt acetate (or manganese acetate), acetic acid, and acetaldehyde, is changed to brown when air or oxygen is passed through the solution, indicating the formation of an intermediate complex, which possibly could catalyze the oxidation of

alcohol. Accordingly, the following experiment was performed: A mixture of 400 cc. glacial acetic acid, 50 cc. water, 30 g. of acetaldehyde, and 10 g. cobalt acetate was treated with oxygen in the stirring apparatus at a temperature of 70-75 deg. C.

Titration of 1 cc. of the starting mixture required 15.67 cc. NaOH; 1 cc. after 2 hours oxidation required 16.07 cc. NaOH; 1 cc. after 7 hours oxidation required 16.08 cc. NaOH; and 1 cc. of a mixture of 400 cc. glacial acetic acid and 50 cc. of water required 16.16 cc. NaOH. It is seen, therefore, that the complete oxidation of the aldehyde is rapidly obtained.

At this point 75 cc. ethyl alcohol were added to the same charge and treatment with oxygen was continued 10 hours. The color remained a bright pink throughout this experiment.

Titration immediately after the addition of the alcohol required 13.92 cc. NaOH. Titration 10 hours later required 13.09 cc.

Then 70 g. more acetaldehyde were added to this mixture of acetic acid and alcohol. The brown color appeared again when oxygen was passed through the mixture. In this case 1 cc. samples were removed at intervals and titrated with 0.959 N NaOH using phenolphthalein as an indicator. Then the acetaldehyde in the 1 cc. sample was determined by adding to the solution from the acid titration 20 cc. of a 20 per cent Na_2SO_3 solution which had been carefully neutralized with phenolphthalein as an indicator. The alkali set free by the reaction of aldehyde with the Na_2SO_3 to form the aldehyde sodium bisulphite compound was then carefully neutralized with standard H_2SO_4 solution.

Titration of 1 cc. samples:

Time of oxidation	Acetic acid	Acetaldehyde
Start	11.46 cc. 0.959 N NaOH	.... cc. 0.979 N H_2SO_4
1½ hours	11.94	2.00
6 hours	12.44	1.32
12 hours	12.82	0.80
21 hours	12.90	0.51
27 hours	12.90	0.49

It is evident from these data that the acetaldehyde is rapidly oxidized to acetic acid, whereas the alcohol present appears to remain unchanged.

Experiment 6

In this experiment another attempt was made to oxidize alcohol catalytically in the absence of acetic acid. The charge at the start was 500 cc. of 95 per cent alcohol and 7 g. manganous acetate. After an 18-hour treatment with oxygen a small amount of cerium acetate was added. After further treatment for 21 hours cobalt acetate was added

and the experiment was continued 38 hours longer. No formation of acetic acid was detected. Schiff's reagent gave a strong positive test for aldehyde, but only 0.2 per cent aldehyde was found by a quantitative determination.

A similar experiment with copper acetate gave no acetic acid.

Experiment 7

In view of the observations of Job and Goard and Rideal that cerium hydroxide in concentrated sodium carbonate solution could catalyze the oxidation of several sugars by air, it appeared desirable to test cerium as a catalyst for alcohol oxidation. On account of the low solubility of sodium carbonate in alcohol, an approximately 2 normal solution of sodium hydroxide was used. A mixture of 500 cc. alcohol, 40 g. NaOH, and 50 cc. of water containing about 5 g. of suspended cerous hydroxide, was treated with oxygen for twelve days at about 70-75 deg. C. Alcohol was added each day to make up for that carried away by the stream of gas. A slight trace of aldehyde was detected in the exit gas. The reaction mixture soon turned to a dark brown and the final product contained several grams of solid aldehyde resin. At the end of the experiment the alcohol was carefully distilled on the water bath. The solid residue was leached with successive portions of water. This water extract was acidified with sulphuric acid and distilled with steam until no further volatile acids came over. The acid content of the distillate was determined, by titrating an aliquot portion, to be 9.52 g. calculated as acetic acid. A determination of the Duclaux constant of the acid distillate gave the following values:

first 10 cc. 6.00 per cent
second 10 cc. 6.39 per cent
third 10 cc. 6.53 per cent

which correspond to a mixture of 70 per cent acetic and 30 per cent formic acids. The salts obtained by neutralizing the acid mixture and evaporating to dryness gave confirmation tests for formic acid: (1) reduction of alkaline permanganate in the cold, (2) reduction of mercuric acetate to mercurous acetate in boiling dilute acetic acid solution, and (3) evolution of carbon monoxide when treated with concentrated H_2SO_4.

There is, therefore, a slow oxidation of alcohol to acetic and formic acids in an alkaline solution containing suspended cerium hydroxide. However, in this alkaline solution the polymerization of acetaldehyde to resin proceeds more rapidly than oxidation of aldehyde to acid, so that the main product is aldehyde resin. Furthermore, no alkaline

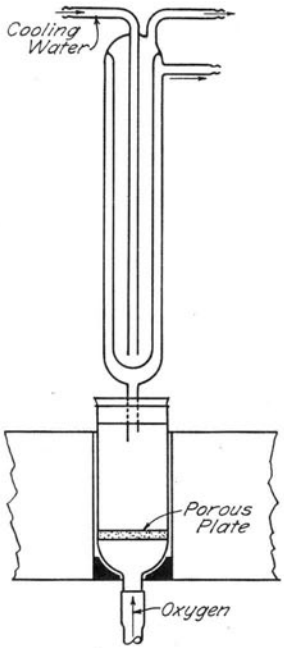


FIG. 2. POROUS PLATE APPARATUS FOR GAS-LIQUID REACTIONS

process would be attractive commercially because of the fact that alkali is consumed in the process and later the acid must be liberated by use of sulphuric acid. For these reasons no further investigation of this reaction was made.

11. *Search for a Catalyst.*—

(a) Apparatus

After having tried the principal catalysts which are known to catalyze the oxidation of acetaldehyde and finding none which would satisfactorily catalyze the oxidation of alcohol alone or in acetic acid solution, it was evident that the next step should be a rather extensive search for a suitable catalyst.

It seemed desirable to develop a more simple apparatus in which catalysts could be tested more rapidly and with the use of much less material. The Schott filter funnel with the sintered glass disc was chosen as the basis of an apparatus which lent itself especially well to the requirements. The apparatus used for testing catalysts is shown in Fig. 2. The alcohol together with the dissolved or suspended

catalyst was contained above the porous plate of the filter funnel. Oxygen was forced upward slowly through the porous plate which broke the gas stream into a multitude of very fine bubbles, thus obtaining intimate contact between the gas and liquid, though probably not as well as with the high-speed stirrer. The top of the funnel was closed with a tin-foil coated rubber stopper through which passed a Hopkins condenser to return as much alcohol as possible from the exit gases. The funnels were surrounded by a steam-heated water bath which maintained the temperature of the alcohol at 70-75 deg. C. A series of eight tests were run simultaneously.

(b) Procedure

One hundred and twenty cc. of C.P. 95 per cent alcohol containing about 1 to 2 per cent of the substance to be tested as a catalyst were poured into the funnel and the oxygen pressure was immediately applied to prevent the liquid from running through the plate. The flow of gas was adjusted by means of a pinch-clamp to give a slow stream of bubbles. After allowing two hours in which to dissolve the catalyst or saturate the alcohol with it, a 10-cc. sample was removed and titrated with 0.1 N NaOH solution, using phenolphthalein as an indicator. After six hours further treatment with oxygen, a second titration was made. Similar titrations were made daily thereafter. Any acetic acid formed would be detected by the quantity of alkali solution required in the titration. The neutralized samples were tested qualitatively for acetaldehyde by means of Schiff's reagent. Alcohol was added daily to keep the volume near its original value. The experiments were continued at least a week on account of the possibility of a period of induction which is characteristic of many autoxidations. At the end of that time the mixture was usually diluted with water until the alcohol concentration was about 30 per cent, and the treatment with oxygen was continued for a couple of days to see if oxidation would take place in dilute solutions. The apparatus was thoroughly cleaned with cleaning mixture, aqua regia, and distilled water between tests.

(c) Materials Tested

The reagents used were of the C.P. grade without further purification. The results of the qualitative tests for aldehyde are given in Table 2. The substances tested are classified according to their positive element and arranged according to the position of this positive element in the periodic systems. The more soluble or homogeneous catalysts are listed first in each column, while the less soluble or heterogeneous catalysts are listed below the other type. In some

cases an odor of acetal was detected. No real evidence of the production of acetic acid appeared in these tests, which were run at atmospheric pressure.

In these experiments it was noticed that in most cases in which the acetate of a metal was used the catalyst would dissolve during the first few hours of the test, forming a clear solution. Then, on further treatment with oxygen a flocculent precipitate, the appearance of which suggested the hydroxide, or basic salt of the metal, formed and increased with time. At the same time, the volume of caustic solution required to titrate a sample of the solution to the phenolphthalein end point decreased abnormally. It was thought at first that this might be due to hydrolysis of the metallic acetate and subsequent evaporation of the acetic acid. However, in later experiments with ozonized oxygen the metal was almost completely precipitated in a few hours, suggesting oxidation of the acetate radical.

12. *Induced Oxidation.*—The attempt made in the preliminary experiments to induce the oxidation of alcohol by oxidation of acetaldehyde in glacial acetic acid was unsuccessful. It appeared desirable, nevertheless, to test other compounds which are known to be readily autoxidized, such as ether and unsaturated hydrocarbons. A series of tests was carried out in the manner described, using a mixture of equal volumes of alcohol and diethyl ether at temperatures in the range 40-50 deg. C. The following substances were tested as catalysts:

Cerium naphthenates
Manganese naphthenates
Copper naphthenates
Nickel naphthenates
Cobalt naphthenates
Iron naphthenates
Phosphotungstic acid
Potassium vanadyl sulphate

The naphthenates were prepared by adding a solution of a salt of the desired metal to a solution of sodium salts of the naphthenic acids from petroleum. The precipitated naphthenates were washed several times with distilled water and dried.

Aldehyde was found in all cases, but no acetic acid formation could be detected.

Similar results were obtained with 10 per cent solutions of pinene and styrene in 50 per cent alcohol and in 95 per cent alcohol, both with and without ferrous sulphate as a catalyst.

13. *Oxidation by Ozone.*—In the experiments with ozone, a stream of oxygen was passed through a laboratory ozonizer of the type made by the U. S. Ozone Company, then through a shellac-lined copper tube to the bottom of one of the Schott filter funnels fitted with a reflux condenser and containing the alcohol and catalyst. Ferric acetate and manganese acetate were tried as catalysts. In both cases the metal precipitated rapidly in a flocculent form resembling the hydroxide. The product had a strong odor of aldehyde and acetal. Titration showed an increase in acidity corresponding to 0.25 per cent by weight calculated as acetic acid in a two-hour experiment. There was no evidence of absorption of unactivated oxygen and appreciable quantities of the ozone passed through the apparatus unchanged.

It was found that alcohol could be oxidized to aldehyde indirectly by ozone in an acid solution of a manganese salt in the following experiment: Manganous sulphate was dissolved in 30 per cent H_2SO_4 solution in a Schott filter funnel and treated with ozonized oxygen at room temperature. The solution turned to a dark red color, indicating the formation of manganic sulphate. On subsequent addition of alcohol and heating, the solution was decolorized, and the alcohol was partially oxidized to acetaldehyde.

Oxidation of alcohol by ozone is not attractive on account of the cost of production of ozone.

14. *Experiments with Ultra-Violet Light.*—In the attempts to oxidize alcohol photochemically, 95 per cent alcohol containing the catalyst was exposed in a quartz flask to the light of a quartz mercury vapor arc lamp. Air was passed through the liquid in a slow stream from a capillary tube extending to the bottom of the flask. The temperature of the alcohol rose to about 30 deg. C. due to the heat radiated from the lamp. The results are given in Table 3. In these experiments a slow oxidation of alcohol to aldehyde and subsequent formation of acetal took place, but no formation of acetic acid could be detected.

15. *Experiments with Internal Heating Coils.*—In all the preceding experiments in which catalysts were tested in the sintered-glass disc funnels, heat was transferred over a large area of surface from a surrounding water bath, the temperature of which was only a few degrees above that of the alcohol. It seemed probable that more thermal activation would be obtained if the heating were done internally by means of an electrical resistance coil of smaller surface area immersed in the mixture of alcohol and oxygen. A further advantage

TABLE 2

ACTION OF CATALYSTS REGARDING ALDEHYDE FORMATION

(Arranged according to the Periodic System)

GROUP I		GROUP II	
Positive	Negative	Positive	Negative
Cupric Acetate	Sodium Xanthate	Beryllium Acetate	Calcium Acetate
Cupric Acetate + Ammonium Acetate	Sodium Sulphite	Magnesium Chloride Hexahydrate	Strontium Acetate
Cupric Acetate + Vanadium Pentoxide	Potassium Tartrate	Zinc Acetate	Cadmium Borotungstate
Cupric Chloride + Ammonium Acetate	Potassium Iodate	Cadmium Acetate	Barium Azide
Cupric Bromide	Lithium Bromide	Cadmium Acetate + Ammonium Acetate	Mercuric Iodide
Silver Nitrate	Lithium Sulphate	Mercuric Acetate	
Sodium Azide	Copper Sulphate + Sulphuric Acid		
Potassium Nitrite	Gold Chloride		
Copper (Metal)	Copper-Silica Gel		Zinc (Metal)
Copper-Zinc Couple	Cupric Acetate + Activated Charcoal		Magnesium (Metal)

GROUP III		GROUP IV	
Positive	Negative	Positive	Negative
Aluminum Acetate	Sodium Perborate	Titanous Sulphate	Germanium Chloride
Indium Nitrate	Boric Acid	Titanium Chloride + Hydrochloric Acid	Zirconium Acetate
Lanthanum Nitrate	Aluminum Chloride	Tin Acetate (Stannous)	Cerium Acetate + Sulphuric Acid
	Aluminum Ethylate	Tin Acetate + Ammonium Acetate	Lead Butyl Mercaptide
	Thallium Acetate	Tin Chloride (Stannous)	Thorium Nitrate
		Tin Acetate + Sulphuric Acid	
		Lead Acetate	
Boron (Amorphous)		Titanium (Metal)	Silica Gel
Aluminum (Metal)		Tin (Metal)	Silica Gel + Sulphuric Acid
Indium (Metal)		Lead (Metal)	Titanic Acid
		Lead Dioxide	Lead (Mossy) (?)

GROUP V		GROUP VI	
Positive	Negative	Positive	Negative
Phosphotungstic Acid	Phosphorus Nitride	Chromous Acetate	Chromium Acetate + Sulphuric Acid
Phosphomolybdic Acid (?)	Vanadium Trichloride	Chromous Acid	Molybdic Acid
Phosphorus Pentoxide	Sodium Arsenite	Chrome Alum in 50% Alcohol	Tellurous Acid
Vanadium Acetate	Potassium Arsenate	Potassium Chromate	Sodium Tungstate
Vanadium Pentoxide	Columbium Chloride	Selenious Acid	Uranium Acetate
Vanadium Pentoxide + Sulphuric Acid	Antimony Pentoxide		Uranium Acetate + Sulphuric Acid
Columbium Chlorate	Potassium Antimonate		Uranic Acid
Columbium Chlorate + Hydrochloric Acid	Tantalum Potassium Fluoride		
Tantalum Chloride	Bismuth Acetate (?)		
Tantalum Chloride + Hydrochloric Acid			Selenium (Powder)
Sodium Bismuthate	Phosphorus (Red)		Tellurium (Powder)
	Antimony (Metal)		Tungstic Acid

TABLE 2.—(*Concluded*)

GROUP VII		GROUP VIII	
Positive	Negative	Positive	Negative
Manganese Acetate	Iodine	Ferric Acetate	Ferric Acetate + Quinhydrone
Manganese Acetate + Sulphuric Acid		Ferric Acetate + Sulphuric Acid	Ferric Citrate
Manganese Acetate + Vanadium Pentoxide		Ferric Acetate + Sodium Acetate	Ferric Tannate
Manganese Acetate + Strychnine		Ferrous Sulphate + Pinene in 50% Alcohol	Ferric Pyrogallate
Manganese Sulphate in 50% Alcohol		Ferrous Sulphate + Styrene in 50% Alcohol	Cobalt Acetate + Sulphuric Acid
		Cobalt Acetate	Nickel Acetate + Sulphuric Acid
		Cobalt Acetate + Ammonium Acetate	Osmic Acid
		Cobalt Acetate + Phosphomolybdic Acid	
		Nickel Acetate	
		Nickel Acetate + Ammonium Acetate	
		Palladium Chloride	
Manganese (Metal)		Iron (Metal)	Iron Oxide (Fe_3O_4)
Manganese Dioxide		Cobalt (Metal)	
		Nickel (Metal)	
		Palladium (Metal)	
		Palladium on Asbestos	
		Ignited Palladium on Asbestos	

ORGANIC COMPOUNDS

Positive	Negative
Chloranil	Hyperol
Benzoyl Peroxide	Quinhydrone
Butyl Nitrite in 50% Alcohol	Azobenzene
	Cupferron
	Styrene (10%)
	Pinene (10%)
Activated Charcoal + Sulphuric Acid	Activated Charcoal

TABLE 3

EXPERIMENTS WITH ULTRA-VIOLET LIGHT

Experiment	Catalyst	Duration hr.	Aldehyde
1	None	3	−
2	Activated charcoal	3½	+
3	4 component hopcalite	8	+
4	Zinc acetate	72	+
5	Uranium acetate	50	+
6	Ferric acetate	24	+
7	Manganous acetate	24	+

TABLE 4
EXPERIMENTS WITH INTERNAL HEATING COIL

Composition of Coil	Catalyst	Duration hr.	Aldehyde	Acid per cent
Chromel	None	24	+	0.01
Chromel	V_2O_5	16	+	....
Chromel	Cobalt Acetate	60	+	....
Platinum	None	48	+	0.003
Platinum	V_2O_5	48	+	....
Platinum	Cobalt Acetate	40	+	....
Oxidized Copper	.....	10	+	....
Oxidized Copper	V_2O_5	120	+	....

would be gained if the metal composing the coil were itself a catalyst such as platinum or copper oxide. The apparatus used was a Schott filter funnel closed with a tin-foil coated rubber stopper through which passed a reflux condenser. The heating coil was located just above the porous plate and was connected between two lead wires sealed into glass tubes. Oxygen was forced through the glass plate, and sufficient current was passed through the heating coil to keep the alcohol near the boiling point.

The experiments are summarized in Table 4.

16. *Use of Aqueous Ferrous Sulphate.*—In order to test the ability of aqueous ferrous sulphate solutions to catalyze the oxidation of alcohol, air was passed in a stream of fine bubbles through a mixture containing 600 cc. water, 300 cc. 95-per-cent alcohol, 75 g. $FeSO_4 7H_2O$, and 40 g. concentrated H_2SO_4. The temperature was maintained at from 80 to 85 deg. C. and the duration of the experiment was 100 hours. At the end of the experiment, 500 cc. of the solution were distilled and an aliquot portion of the distillate was titrated with standard alkali solution. Fifty cc. of the distillate required 0.32 cc. of N/10 NaOH. Calculated as acetic acid, the result would correspond to only 0.004 per cent. A qualitative test with Schiff's reagent indicated the presence of aldehyde. There is then an extremely slow oxidation giving acetaldehyde as the chief product.

17. *Oxidation under Pressure.*—In order to obtain the advantage of increased thermal activation at higher temperatures and still retain the temperature-regulating benefit of the liquid phase, it is necessary to use higher pressures. A further advantage to be gained by the use of higher pressures is that the concentration of oxygen dissolved in the liquid phase increases almost proportionally with the absolute pressure, and the rate of conversion should be accordingly increased.

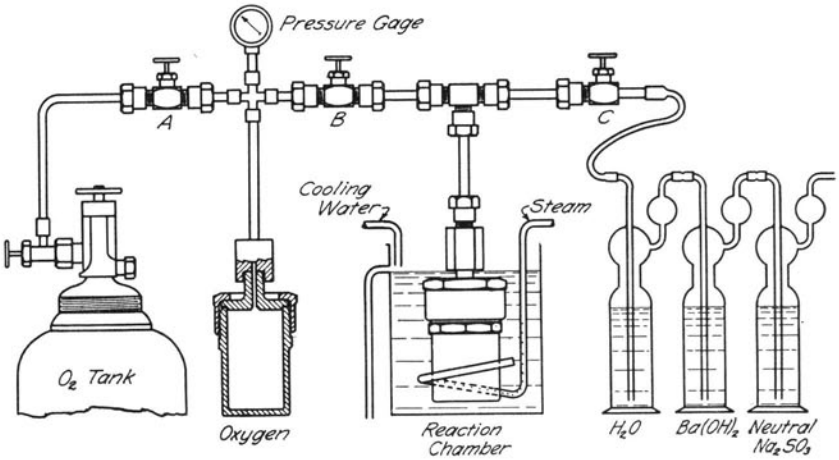


FIG. 3. APPARATUS FOR PRESSURE OXIDATION

In the case of such mixtures of oxygen and an inflammable compound, however, the danger of serious explosions increases rapidly as the pressure is increased. The following experiments were made to study the oxidation of alcohol under a moderately increased pressure and temperature (100 deg. C.).

The apparatus used is shown diagrammatically in Fig. 3. The reaction chamber was a modified Parr oxygen bomb in which the rubber gasket was replaced by one of lead. It was connected by standard high pressure connections to a second Parr oxygen bomb which was used only as an intermediate oxygen container for the purpose of safety. The reaction chamber was surrounded by a boiling water bath heated by steam jets. As a matter of precaution, both bombs were enclosed by a heavy steel shield. A, B, and C are needle valves which were operated by extension handles passing through the top of the steel box.

The catalyst to be tested was dissolved or suspended in the alcohol. A 10 cc. sample of the mixture was titrated as a control with 0.1 N sodium hydroxide using phenolphthalein as an indicator. A similar 10 cc. portion of the mixture was placed in a beaker within the reaction chamber which was then closed tightly and connected as shown in the diagram. Valve B was closed, valve A was opened, and the oxygen container was filled with oxygen from the tank to a pressure twice as great as that desired in the reaction chambers. Most of the experiments were performed with an oxygen pressure of 170 lb. per sq. in. (11.3 atmospheres) at room temperature. Under

TABLE 5
OXIDATION UNDER PRESSURE AT 100 DEG. C.

Catalyst	O_2 Pressure lb. per sq. in. at 25 deg. C.	Time hr.	Per Cent Conversion		
			To aldehyde	To acid	To CO_2
None	170	24	trace	0.027	0.0
Cerous hydroxide in Na_2CO_3 solution	170	24	....	0.26	...
Ferric ferrocyanide in absolute alcohol	160	40	0.63	0.045	...
4-component hopcalite in absolute alcohol	170	24	trace	0.64	0.5
2-component hopcalite in 95 per cent alcohol	170	24	0.21	0.068	0.3

this pressure, the reaction chamber contained just the amount of oxygen theoretically required to oxidize the 10 cc. of alcohol to acetic acid. Valve A was then closed, and the tank of high pressure oxygen was disconnected from the system. Valve C was closed and valve B was then opened sufficiently to allow the pressure to equalize in the two bombs. It was then closed. The bath was heated for the desired length of time, usually 24 hours, at 100 deg. C., then the steam was turned off and the bomb cooled to room temperature before the pressure was released. The exit gases were passed slowly through scrubbing bottles containing, respectively, water to remove most of the acid and aldehyde, barium hydrate solution for the qualitative indication and removal of CO_2, and neutral sodium sulphite for the removal of the last traces of aldehyde. The contents of the first bottle were titrated with 0.1 N sodium hydroxide, then the neutral sodium sulphite in the third bottle was added and the base liberated by aldehyde was titrated with 0.1 N sulphuric acid.*

The liquid residue in the bomb, which usually amounted to 8 cc., was titrated similarly for acid and for aldehyde. In cases where the quantity of aldehyde was too small to determine by the method of Seyewitz and Bardin, a qualitative test was made on the neutralized liquid residue with Schiff's reagent.

The results with about forty of the substances previously tested as catalysts were closely parallel to those obtained with the same substances at atmospheric pressure and 70-75 deg. C. These substances included the acetates of metals, such as cobalt, manganese, iron, tin, uranium, copper, silver, thallium, lead, cerium, etc., and solids such as copper bronze, silica gel, and activated charcoal. In most cases there was no detectable formation of carbon dioxide or acetic acid, and the aldehyde content of the residue was rarely greater

*Seyewitz and Bardin, Bull. Soc. chim. 3, 33, 1000, 1905.

than that required to give a qualitative test with Schiff's reagent. In many cases the odors of paraldehyde and acetal were detected. However, in the case of four of the solid catalysts tested, namely, cerous hydroxide in a saturated solution of Na_2CO_3 in 50 per cent alcohol, ferric ferrocyanide in absolute alcohol, and hopcalite catalysts prepared by the methods of Merrill and Scalione,* measurable quantities of acid and aldehyde were produced.

These hopcalites have approximately the following percentage composition:

Four-Component		Two-Component	
MnO_2	50	MnO_2	60
CuO	30	CuO	40
CO_2O_3	15		
Ag_2O	5		

The quantity used in each experiment was about 1 g. in 10 cc. of alcohol.

The results obtained in the first experiments are shown in Table 5.

Further experiments were then made to ascertain the mechanism of the reaction with the hopcalite catalysts and if possible to increase the conversion to acid and aldehyde.

The first question to be answered was whether the oxidation in the presence of hopcalites is truly catalytic, or whether it is principally a chemical oxidation in which some of the oxides of the hopcalite are simultaneously reduced to the corresponding free metals. If the latter is the true mechanism, then the reaction should take place just as well in the presence of an inert gas. Accordingly, samples of alcohol and hopcalites were heated for various lengths of time in a bomb from which the air had been displaced by nitrogen. Under these conditions the only free oxygen present would be that adsorbed by the hopcalite and in solution in the alcohol. The data from these tests are shown in Table 6. These results might be due either to a chemical oxidation by the metallic oxides or to a catalytic oxidation by oxygen adsorbed on the surface of the catalyst.

Inasmuch as water vapor is an active poison for hopcalites in the catalytic oxidation of carbon monoxide, it was expected that much better results could be obtained with absolute alcohol than with ordinary 95 per cent alcohol. However, the results of the experiments in Table 7 do not show a consistent difference between the results obtained by the two grades of alcohol.

In order to determine whether the reaction is slow, or whether it takes place rapidly at first, and then decreases in speed until a steady

*Merrill and Scalione, J. Am. Chem. Soc., 43, 1982, 1921.

TABLE 6
REACTION OF HOPCALITES AND ALCOHOL IN NITROGEN

Catalyst Component	Alcohol	Time hr.	Per Cent Conversion	
			To aldehyde	To acid
2	absolute	24	0.23	....
2	absolute	68	0.30	0.01
2	absolute	72	0.23	0.015
4	absolute	48	0.26	0.025
4	absolute	192	0.91	0.27
4	absolute	192	0.91	0.02

TABLE 7
COMPARISON OF RESULTS WITH 95 PER CENT ALCOHOL AND ABSOLUTE ALCOHOL

Catalyst Component	Alcohol	O_2 Pressure lb. per sq. in. at 25 deg. C.	Time hr.	Per Cent Conversion	
				To aldehyde	To acid
2	95 per cent	170	24	....	0.049
2	95 per cent	170	24	0.68	0.05
2	95 per cent	170	24	0.23	0.07
2	95 per cent	170	24	0.21	0.068
2	95 per cent	170	72	0.80	0.13
2	absolute	170	24	0.17	0.07
2	absolute	170	24	....	0.09
4	absolute	170	24	....	0.64
4	absolute	200	24	0.17	0.44

state is reached, some tests were made to study the effect of the time of heating on the formation of aldehydes and acid. The results are shown in Table 8.

These results indicate that the formation of aldehyde takes place rather rapidly at first, but the aldehyde soon reaches a concentration beyond which there is very little increase with time. The formation of acid is apparently very slow at the beginning and takes place over a longer period of time.

One possible explanation of this apparent maximum concentration of aldehyde is that the hopcalite becomes poisoned and no longer functions as catalyst for aldehyde formation. In order to test this possibility, several runs were made using the same catalyst. At the end of each run the liquid residue was separated by filtration and was analyzed. The catalyst was immediately transferred to a fresh sample of alcohol for a new run. The data of these tests are shown in Table 9.

TABLE 8
EFFECT OF TIME OF HEATING

Catalyst Component	Alcohol	O_2 Pressure lb. per sq. in. at 25 deg. C.	Time hr.	Per Cent Conversion	
				To aldehyde	To acid
4	absolute	100	2	0.68	0.000
4	absolute	100	4	0.77	0.022
4	absolute	100	14	0.91	0.056
4	absolute	150	2	0.85	0.000
4	absolute	150	6	0.65	0.025
4	absolute	150	14	0.65	0.028

TABLE 9
BEHAVIOR OF THE SAME CATALYST IN REPEATED TESTS
Four-component hopcalite

Run	Catalyst Sample	Alcohol	O_2 Pressure lb. per sq. in. at 25 deg. C.	Time hr.	Per Cent Conversion	
					To aldehyde	To acid
1	1	absolute	200	24	0.91	0.48
2	1	absolute	200	24	1.20	0.36
3*	2	absolute	200	24	0.77	0.36
4	2	absolute	200	24	0.97	0.28
5	2	absolute	200	24	1.08	0.40

*Runs 3, 4, and 5 were not made with the same catalyst used in 1 and 2.

These results would appear to indicate that the limiting of the conversion to aldehyde is due to the concentration of some material in the liquid phase rather than to some deficiency of the catalyst. Some of the oxidation products may act as inhibitors.

A series of similar experiments was then made using the same sample of catalyst for seventeen consecutive runs. At the end of the 5th, 8th, 14th, 15th, and 16th runs, the catalyst was heated to a dull red heat in an open crucible and allowed to cool in the air. The results are shown in Table 10. Apparently, there is some increase in activity due to heating in air, but it is not very great.

It was thought that the conversion of ethyl alcohol to aldehyde and acid could be accomplished by hopcalite in a two-step process, in the first step of which the alcohol is partially oxidized chemically by the hopcalite, and in the second the hopcalite is separated and regenerated by heating in oxygen. By repeating this cycle a number of times with the same sample of alcohol, it might be possible to increase the concentrations of acid and aldehyde considerably.

TABLE 10
REACTIVATION OF CATALYST BY HEATING
Four-component hopcalite in absolute alcohol

Run	O_2 Pressure lb. per sq. in. at 25 deg. C.	Time hr.	Per Cent Conversion	
			To aldehyde	To acid
1	160	24	0.28	0.04
2	160	24	0.97	0.08
3	160	48	0.33	0.10
4	160	24	0.57	0.08
5	160	24	0.34	0.06
6*	160	24	1.03	0.24
7	160	24	1.48	0.26
8	160	24	0.96	0.57
9*	100	24	1.54	0.24
10	100	24	0.46	0.25
11	100	24	1.02	0.23
12	100	24	0.85	0.20
13	100	24	0.85	0.07
14	100	24	0.68	0.11
15*	100	24	1.14	0.20
16*	100	24	0.91	0.29
17*	100	24	0.80	0.25

*Before these runs were made catalyst was heated to dull red and cooled in air.

Accordingly, a 50 cc. sample of absolute alcohol and 10 grams of two-component hopcalite were heated two hours with oxygen at 170 pounds pressure. The catalyst was then separated and heated to a red heat and cooled in air. This procedure was repeated several times with the same sample of alcohol. Analysis of the mixture showed that a considerably greater weight of aldehyde and acid had been formed, but, owing to the larger mass of the sample, the percentage conversions were no larger than those obtained in previous experiments. Similar experiments with an atmosphere of nitrogen in the bomb, instead of oxygen, gave about the same results.

The experimental results shown in Table 11 were obtained by heating 10 cc. of absolute alcohol with a sufficiently large quantity of two-component hopcalite to hold all the alcohol on its surface without leaving any free liquid phase. At the end of each experiment, the gases were analyzed as before and the remainder of the oxidation products were washed out of the hopcalite and analyzed. The hopcalite was then dried and was used again in the next experiment. After the third experiment it was heated to a dull red heat and cooled in air.

The percentage conversion to aldehyde and acid are increased somewhat by this procedure.

TABLE 11
OXIDATION OF ALCOHOL ADSORBED BY HOPCALITE

Experiment	O_2 Pressure lb. per sq. in. at 25 deg. C.	Time hr.	Per Cent Conversion	
			To aldehyde	To acid
1	160	24	....	0.45
2	160	22	1.31	0.90
3	160	22	1.53	1.28
4*	160	48	1.13	1.06

*Before this experiment was made hopcalite was heated and cooled in air.

V. CONCLUSIONS

18. *Conclusions.*—A catalytic study, using approximately one hundred and fifty different catalysts, of the air oxidation of ethyl alcohol in the liquid phase proved that it was quite possible to partially oxidize the ethyl alcohol to acetaldehyde.

A study was not only made of the various catalysts which would affect this oxidation, but also of various conditions under which this reaction could be made to take place.

Similar results were obtained in attempts to oxidize alcohol under pressure at 100 deg. C. with dissolved catalysts, and with several solid catalysts.

Hopcalite catalysts, however, produced measurable quantities of aldehyde and acid, but no way was found to increase the conversion to either product much above one per cent.

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